Structure of Au Nanoclusters on TiO_2(110) Surface Studied by Polarization Dependent Total-Reflection Fluorescence (PTRF) XAFS

Satoru Takakusagi[1], Kotaro Miyazaki[1], Naoki Watanabe[1], Wang-Jae Chun[2], Yuichiro Koike[1], Masaharu Nomura[3], Kaoru Ijima[4] and Kiyotaka Asakura[1]

[1]Catalysis Research Center, Hokkaido University, Sapporo 001-0021, Japan , [2]Chemistry Department, International Christian University, Mitaka 181-8585, Tokyo, Japan, [3]Photon Factory, Institute of Materials Structure Science, Tsukuba 305-0801, Japan, [4]Yamanashi University, Kohu 400-8510, Yamanashi, Japan,

FAX: +81-11-706-9114, E-mail: takakusa@cat.hokudai.ac.jp

1. Introduction

Metal/oxide systems play a major role in many technological applications such as heterogeneous catalysts, electronic devices and gas sensors. Heterogeneous catalysts are usually used as metal nanoclusters supported on metal oxide surfaces. In particular gold nanoclusters on TiO_2 with less than 10 nm show extraordinary high activity towards CO oxidation reactions at low temperature.[1)] In this study we examined the structure of Au nanoclusters on TiO_2(110) single crystal surface by using Polarization Dependent Total-Reflection Fluorescence (PTRF) XAFS to elucidate the interaction between Au and TiO_2 and the origin of catalytic properties of nano-sized Au.

2. Experimental

EXAFS measurements were carried out at BL9A in Photon Factory (KEK-PF, Japan) using a home-made PTRF-XAFS system.[2, 3)] TiO_2(110) surface was cleaned by cycles of Ar ion sputtering and annealing at 1000 K, and Au was vacuum-deposited on TiO_2(110) in an UHV preparation chamber of the PTRF-XAFS system. The polarization dependent measurements of XAFS were performed in 3 different directions using 6-axis goniometer. XAFS analysis was carried out using REX 2000 (Rigaku Co.) and FEFF8.0 softwares.

3. Results and Discussion

Fig.1(a) shows the polarization dependent EXAFS oscillations of Au on TiO_2(110) at a low coverage (4.1×10^{13} atoms/cm^2). There were no significant differences in all the orientations, indicating structure of the deposited Au should be a symmetric one. Amplitude of the observed EXAFS oscillations was much smaller than that of the standard Au foil sample, which suggested that Au species were in a lower coordination state. These results indicated formation of small Au nanoclusters in a symmetric shape. In addition the Au-Au bond length was found to be 2.78 Å which was shorter than that of bulk Au. Theoretical EXAFS oscillations were calculated to determine the structure of the Au nanoclusters. We obtained a well-fitted result when assuming a fcc-cuboctahedral Au nanocluster with 13 gold atoms (Fig.1 (a), (b)). .

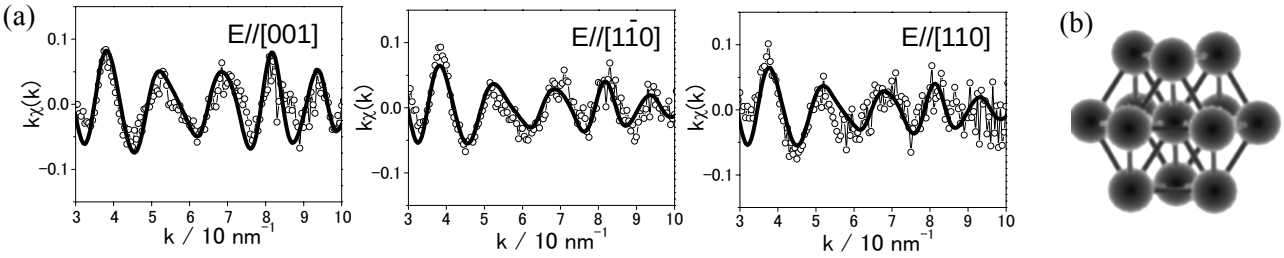

Fig. 1 (a) Polarization dependent Au L_{II} edge XAFS spectra. Dots and thick lines are observed and calculated EXAFS oscillations, respectively. (b) Structure of Au nanocluster used for theoretical calculation in (a).

References

1) M. Haruta, *Catal. Survyes Jpn*. **1** (1997) 61.

2) W.-J. Chun, Y. Tanizawa, T. Shido, Y. Iwasawa, M. Nomura, K. Asakura, *J. Synchrotron Rad.* **8** (2001) 168.

3) Y. Koike, K. Fujikawa, S. Suzuki, W.-J. Chun, K. Ijima, M. Nomura, Y. Iwasawa, K. Asakura, *J. Phys. Chem*. C, **112** (2008) 4667.